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㉚ **Herbicide emulsifiable suspension concentrate compositions.**

㉛ There are provided compositions of a concentrated amount of an herbicidally active agent, or combination of agents, in a solid state suspended in a water immiscible solvent containing an anionic surfactant and a nonionic surfactant and optionally containing an antifoam agent and a suspending or thickening agent. Upon dilution with hard or soft water, said compositions readily form sprayable herbicidal emulsions.

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HERBICIDAL EMULSIFIABLE SUSPENSION CONCENTRATE COMPOSITIONS

This invention relates to novel and useful agricultural formulations of herbicidal agents which exhibit poor solubility characteristics in both aqueous and organic media.

It is an object of this invention to provide an emulsifiable suspension concentrate composition of the free acids of a herbicidal agent, such as N-phosphonomethylglycine and 2-(imidazolin-2-yl)pyridine carboxylic acids, without the pre-formulation of the corresponding herbicidal salts. It is an object of this invention to produce herbicidal compositions which are physically stable and readily dilutable in hard or soft water to give a sprayable herbicidal emulsion.

The present invention relates to a novel emulsifiable suspension concentrate composition of a herbicidal agent characterized by a relative degree of insolubility in both aqueous and non-aqueous media. The emulsifiable suspension concentrate composition of the invention is comprised of an active herbicidal agent, or combination of agents, in a solid state suspended in a water immiscible solvent containing an anionic surfactant and a nonionic surfactant and optionally containing an antifoam agent and a suspending or thickening agent.

The water immiscible solvent is a non-paraffinic heavy aromatic solvent consisting of a mixture of aromatic hydrocarbons, such as naphthalenes and alkylnaphthalenes, having a distillation range of about 118° to 305°C.

The above-described compositions allow the formulation of active herbicidal agents such as amino acids and imidazolinyl nicotinic acids without further chemical modifications, such as salt or ester formation. The above compositions provide a stable, concentrated, readily dilutable form of a herbicide suitable for spray application. The compositions also exhibit surprising herbicidal efficacy comparable to the efficacy of the corresponding salts.

The present invention also relates to an emulsifiable suspension concentrate composition of a herbicidal agent comprising an amino acid or imidazolinylpyridine carboxylic acid (alone or in combination) in a solid state suspended in a water immiscible liquid containing an anionic surfactant and an ethoxylated fatty acid surfactant and optionally containing an antifoam agent and a thickening or suspending agent.

The herbicidal agent is usually sold in a concentrated form either as a solid or a liquid and, just prior to application, the concentrate is diluted with water, or water containing adjuvants, and sprayed on fields of soil and/or actively growing plants. Solid concentrate formulations, such as granulars, wettable powders and dusts, may also be used.

Since not all solid concentrate formulations of the free acid form of herbicidal agents, such as N-phosphonomethylglycine, exhibit the same high magnitude of efficacy and further since certain highly effective herbicidal compounds, such as N-phosphonomethylglycine and imidazolinyl nicotinic acids, are relatively insoluble in water and conventional organic solvents, they are not readily amenable to commercial formulation. Chemical modification of said compounds to give the corresponding salts is required to improve their solubility characteristics. Surprisingly, it has been found that compounds, such as amino acids and imidazolinyl nicotinic acids, may be formulated as liquid concentrates without further chemical modifications of said compounds and with a high degree of retention of efficacy.

The emulsifiable suspension concentrate compositions of the present invention are comprised of about 10% to 50% of a herbicidal agent, such as N-phosphonomethylglycine or an imidazolinyl nicotinic acid, alone or in combination, suspended in about 29% to 84% of a non-paraffinic aromatic solvent mixture having a distillation range of 118° to 305°C containing about 3% to 10% of an anionic surfactant, about 3% to 10% of an ethoxylated fatty acid surfactant, 0 to about 0.10% of an antifoam agent and 0 to about 2.0% of a suspending or thickening agent.

One preferred composition comprises about 30% to 50% of an active herbicidal agent or combination of agents, about 40% to 57% of a non-paraffinic aromatic solvent mixture having a distillation range of 118° to 305°C, about 5.0% to 7.0% of an anionic surfactant, about 5.0% to 7.0% of an ethoxylated fatty acid surfactant, about 0.02% to 0.15% of an antifoam agent and 0.5 to 2% of a suspending agent.

Among the herbicidal agents suitable for use in the compositions of the invention are amino acids such as glyphosate and imidazolinylpyridine carboxylic acids such as imazapyr and combinations thereof. A preferred herbicidal agent is glyphosate, alone or in combination with an imidazolinyl nicotinic acid.

Solvents suitable for use in the compositions of the invention include heavy aromatic solvent mixtures having a distillation range of 118° to 305°C. Preferred solvents include those mixtures of aromatics having a distillation range of about 183° to 285°C, and the most preferred aromatic solvent mixtures is that which distills in a range of about 225° to 280°C. Anionic surfactants suitable for use in the present invention include alkylarylsulfonic acids such as C₈-C₁₈ alkylbenzenesulfonic acid, with dodecylbenzenesulfonic acid

being the preferred anionic surfactant.

Among the ethoxylated fatty acid surfactants which may be employed are ethoxylated castor oils with about 15-60 ethylene oxide units per molecule. Preferred ethoxylated castor oils are those which have about 36-40 ethylene oxide units per molecule. Suitable antifoam agents include silicone polymers containing silica such as dimethylsilicone polymer plus silica, and suitable suspending or thickening agents include hydrated fumed silica or attapulgite clays or amine treated attapulgite clays.

The herbicidal emulsifiable suspension concentrate compositions may be prepared by dissolving an anionic surfactant in an aromatic solvent and adding a solid herbicidal agent or combination of agents, with vigorous agitation to form a suspension. This suspension is milled to the required particle size distribution. A median particle diameter of 1-2 microns provides suitable physical properties. The milled suspension is treated with an ethoxylated fatty acid surfactant and, optionally, an antifoam agent and a suspending or thickening agent and mixed thoroughly. Alternatively, the herbicidal agent is milled as a dry powder and is added to a solution of the anionic surfactant in the aromatic solvent with vigorous agitation to ensure complete dispersion and the remaining components are added with stirring.

The above-prepared emulsifiable suspension concentrate compositions are physically stable and demonstrate excellent dilution properties in hard and soft waters to produce a sprayable herbicidal emulsion. In practice, it is generally preferable to dilute the compositions of the invention in water containing about 0.25% of an adjuvant such as a polyoxyethylene sorbitan laurate surfactant to obtain an especially high degree of herbicidal activity.

In order to facilitate a further understanding of the invention, the following examples are presented primarily for the purpose of illustrating certain more specific details thereof. Unless otherwise noted, all parts are by weight.

EXAMPLE 1	
Preparation of an N-phosphonomethylglycine emulsifiable suspension concentrate composition	
Component	%
N-phosphonomethylglycine	41.90
Dodecylbenzenesulfonic acid	6.00
Ethoxylated castor oil, 36C ¹	6.00
Dimethylsilicone polymer with silica ²	0.10
Mixture of aromatic hydrocarbons with a distillation range of 226°-279°C ³	46.00
	100.00

1. 36 units of ethylene oxide per molecule Flomo® 36C, manufactured by DeSoto

2. TH 100IND® antifoam, manufactured by Thompson-Hayward

3. Aromatic 200®, manufactured by EXXON

Method 1

An anionic surfactant, dodecylbenzenesulfonic acid, is dissolved in a water immiscible solvent, Aromatic 200®, with stirring. This solution is treated with the herbicidal agent, N-phosphonomethylglycine, in a crystalline or powder state with vigorous stirring to give a dispersion. The resultant dispersion is milled until a median particle size of 1-2 microns is obtained.

The milled dispersion is treated with an ethoxylated fatty acid surfactant, castor oil, 36C¹, and an antifoam agent, dimethylsilicone polymer with silica² and mixed thoroughly.

Method 2

The herbicidal agent, N-phosphonomethylglycine, is milled to give a median particle size of 1-2 microns and then added to a solution of an anionic surfactant, dodecylbenzenesulfonic acid in a water immiscible solvent, Aromatic 200®, with vigorous agitation. The resultant dispersion is treated with an ethoxylated fatty acid surfactant, castor oil, 36C¹, and an antifoam agent, dimethylsilicone polymer plus silica², and mixed thoroughly.

Physical Properties

The physical characteristics of the above-described N-phosphonomethylglycine emulsifiable concentrate composition are shown below.

Viscosity (Brookfield LVT at 22°C spindle #2, speed 30 rpm)	500-600 cP
Density at 20°C	1.41 g/mL
Particle size (Horiba CAPA 700)	1.21 microns (median)
pH, 2% diluted in deionized water	2.0-2.4
Dispersibility in water (in both standard hard and soft waters), 2.5 g in 100 ml total volume.	Good emulsification, no oil separation after 24 hours.

EXAMPLE 2Preparation of 2-(imidazolin-2-yl)nicotinic acid emulsifiable suspension concentrate compositions

<u>Components</u>	<u>A</u>	<u>B</u>
Imazethapyr	-	33.3
Imazapyr	33.33	-
Dodecylbenzenesulfonic acid	5.00	5.00
Ethoxylated castor oil, 36C ¹	5.00	5.00
Dimethylsilicone polymer with silica ²	0.03	0.03
Mixture of aromatic hydrocarbons with a distillation range of 226°-279°C	56.64	56.64
	100.00	100.00

1. 36 units of ethylene oxide per molecule Flomo® 36C, manufactured by DeSoto

2. TH IND30® antifoam, manufactured by Thompson-Hayward

3. Aromatic 200®, manufactured by EXXON

Method

The herbicidal agent, as a finely divided powder, is added to a rapidly stirred solution of the anionic surfactant, dodecylbenzenesulfonic acid, in the aromatic solvent, Aromatic 200®. The resultant dispersion is treated with the remaining components and placed on a high shear mixer for 3 minutes.

Optionally the solid herbicidal agent is milled to a median particle size of 1-2 microns prior to use in the above-described preparation.

<u>Physical Properties</u>	<u>A</u>	<u>B</u>
Dispersibility in water, 4.0 g in 100 ml total volume.	Good emulsification, slight settling after 24 hours, easily resuspended	Good emulsification, slight settling after 24 hours, easily resuspended

EXAMPLE 3**Preparation of combination emulsifiable
suspension concentrate compositions**

Components	C	D
Glyphosate	37.69	32.89
Imazapyr	4.20	9.00
Dodecylbenzenesulfonic acid	6.00	6.00
Flomo® 36C ¹	6.00	6.00
TH 100IND® antifoam ¹	0.10	0.10
Aromatic 200® ¹	46.01	46.01
	100.00	100.00

1. As described in Example 1.

Method

A solution of dodecylbenzene in Aromatic 200® is treated with glyphosate with rapid stirring. The resultant dispersion is treated with the remaining components and placed on a high shear mixer for 3 minutes.

Optionally, a dispersion of glyphosate and the imidazolinyl nicotinic acid solid in a solution of dodecylbenzenesulfonic acid in Aromatic 200® is milled to give a median particle size of 1-2 microns prior to the addition of the remaining components.

Physical Properties	C	D
Dispersibility in water, 4.0 g in 100 ml total volume.	Good emulsification, slight oil separation after 24 hours, easily resuspended	Good emulsification, slight oil separation after 24 hours, easily resuspended

EXAMPLE 4**Greenhouse Postemergent Herbicidal Evaluation**

This is an evaluation of the postemergent herbicidal activity of the emulsifiable suspension concentrate composition of N-phosphonomethylglycine as compared to a commercial aqueous solution composition of the isopropylammonium salt of N-phosphonomethylglycine.

The test compositions used for this evaluation are the emulsifiable suspension concentrate composition of N-phosphonomethylglycine which is described in Example 1 and referred to herein as Glyphosate 40 ESC and an aqueous soluble composition of the isopropylammonium salt of N-phosphonomethylglycine which is commercially sold by Monsanto under the trademark ROUNDUP® and referred to herein as Glyphosate Salt.

Seedling plants are grown in jiffy flats for about 2 weeks. The glyphosate 40 ESC composition is dispersed in water containing 0.25% TWEEN-20®, a polyoxyethylene sorbitan monolaurate surfactant manufactured by Atlas Chemical Industries in sufficient quantity to provide the equivalent of about 0.063 kg to 0.500 kg per hectare of N-phosphonomethylglycine to the plants when applied through a spray nozzle operating at 40 psi for a predetermined time. The Glyphosate Salt is dispersed in water according to the label directions and applied to the plants as described above. After spraying, the plants are placed on greenhouse benches and cared for in the usual manner commensurate with conventional greenhouse practices. The plants are evaluated at 7 and 14 days after treatment and rated according to the rating system shown below.

Rating System	% Control
No effect	0
Possible effect	1-10
Slight effect	11-25
Moderate effect	26-40
Definite injury	41-60
Herbicidal effect	61-75
Good Herbicidal effect	76-90
Approaching complete kill	91-99
Complete kill	100

Plant Species Used	
Common Name	Scientific Name
Mustard Wild	Brassica kaber
Cotton	Gossypium hirsutum
Corn	Zea mays
Morningglory	Ipomoea purpurea
Soybean	Glycine max
Barnyard Grass	Echinochloa crus-galli
Lambsquarters	Chenopidium album
Ragweed	Ambrosia artemisifolia
Green Foxtail	Setaria veridis

The data obtained at 14 days after treatment are reported in Table 1 below.

Table I

Postemergence Herbicidal Evaluation										
Composition	Rate (kg/ha)	Mustard	Cotton	Field Corn	Morn gly	Soybean	Barnyardg	Lambsquart	Rag weed	Gm Foxtail
Glyphosate Salt	0.500	80.0	80.0	90.0	66.7	78.3	98.7	99.3	38.3	100.0
Glyphosate ESC	0.500	60.0	50.0	95.0	71.7	80.0	94.3	96.3	40.0	91.7
Glyphosate Salt	0.250	38.3	35.0	58.3	63.3	63.3	71.0	83.3	33.3	85.0
Glyphosate ESC	0.250	33.3	40.0	85.3	75.3	71.7	78.3	100.0	53.3	93.3
Glyphosate Salt	0.125	13.3	20.0	18.3	30.0	20.0	23.3	61.7	6.7	46.7
Glyphosate ESC	0.125	26.7	3.3	71.7	30.0	50.0	48.3	83.3	23.3	81.7
Glyphosate Salt	0.063	0.0	3.3	3.3	15.0	6.7	16.7	36.7	0.0	20.0
Glyphosate ESC	0.063	6.7	0.0	61.7	10.0	20.0	35.0	70.0	13.3	40.0

EXAMPLE 5

Field Postemergent Herbicidal Evaluation

The test compositions used are glyphosate 40 ESC and Glyphosate Salt, and are as described in Example 4.

A field containing established, actively growing plants is divided into plots of 10 meters x 30 meters and is sprayed with a tractor mounted compressed air sprayer with a delivery of 200 liters per hectare. The

Glyphosate 40 ESC composition is dispersed in water containing 0.25% TWEEN-20® in sufficient quantity to provide the equivalent of 2.0 kg to 0.5 kg per hectare to the plants. Glyphosate Salt is dispersed in water according to the label directions and applied to the plants as described hereinabove. The plots are evaluated at 7 and 14 days after treatment. Each treatment is replicated once. The data obtained for 14 days after treatment is reported in Table II.

Plant Species Used	
Common Name	Scientific Name
Redroot pigweed	<i>Amaranthus retroflexus</i>
Common lambsquarters	<i>Chenopodium album</i>
Common purslane	<i>Portulaca oleracea</i>
Common ragweed	<i>Ambrosia artemisiifolia</i>
Large crabgrass	<i>Digitaria sanguinalis</i>
Fall panicum	<i>Panicum diploteris</i>
Barnyard grass	<i>Echinochloa crus-galli</i>
Foxtail millet	<i>Setaria italica</i>

Table II

Postemergence Field Evaluation								
Composition	Rate (kg/ha)	Red Root Pigweed	Lambsquart	Ragweed	Crab grass	Fall pani	Barnyardg	Foxtail millet
Glyphosate Salt	0.5	100	80	98	100	95	100	100
Glyphosate ESC	0.5	100	100	85	100	98	100	100
Glyphosate Salt	1.0	100	100	100	100	100	100	100
Glyphosate ESC	1.0	100	100	100	100	100	100	100
Glyphosate Salt	2.0	100	100	100	100	100	100	100
Glyphosate ESC	2.0	100	100	100	100	100	100	100

Claims

1. A suspension concentrate composition for a herbicidal agent characterized by a herbicidal agent containing a free carboxylic acid moiety, a water immiscible solvent, an anionic surfactant, a nonionic surfactant and optionally an antifoam agent and a suspension agent.
2. The composition according to Claim 1 wherein the herbicidal agent is selected from the group consisting of derivatives of amino acid, derivatives of pyridine carboxylic acid and combinations thereof.
3. The composition according to Claim 2 wherein the herbicidal agent is N-phosphonomethylglycine.
4. The composition according to Claim 2 wherein the herbicidal agent is selected from the group consisting of 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid, 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid and 5-methyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid.
5. The composition according to Claim 1 wherein the herbicidal agent is N-phosphonomethylglycine in combination with a pyridine carboxylic acid derivative.
6. The composition according to Claim 2 wherein the water immiscible solvent is an aromatic hydrocarbon mixture having a distillation range of 118°C to 305°C, the anionic surfactant is a C₈-C₁₈ alkylbenzenesulfonic acid and the nonionic surfactant is ethoxylated castor oil with 15-60 ethylene oxide units per molecule.
7. The composition according to Claim 3 wherein the water immiscible solvent is an aromatic hydrocarbon mixture having a distillation range of 183°C to 285°C, the anionic surfactant is dodecylbenzenesulfonic acid and the nonionic surfactant is ethoxylated castor oil with 36-40 ethylene oxide units per molecule.
8. The composition according to Claim 7 characterized by 10.0% to 50.0% of N-phosphonomethylglycine, 29.0% to 84.0% of an aromatic hydrocarbon mixture having a distillation range of 183°C to 285°C 3.0% to

10.0% of dodecylbenzenesulfonic acid, 3.0% to 10.0% ethoxylated castor oil with 36 ethylene oxide units per molecule, 0 to 0.10% of an antifoam agent and 0 to about 2.0% of a suspension agent.

9. The composition according to Claim 4 characterized by 30.0% to 50.0% of the herbicidal agent, 40.0% to 60.0% of an aromatic hydrocarbon mixture having a distillation range of 183° to 285°C, 4.0% to 8.0% of an anionic surfactant, 4.0% to 8.0% of an ethoxylated castor oil having 10-60 units of ethylene oxide per molecule and 0 to about 2.0% of an antifoam agent.

10. The composition according to Claim 5 characterized by 30.0% to 40.0% of N-phosphonomethylglycine in combination with 0.5% to 10.0% of a pyridine carboxylic acid derivative, 45.0% to 60.0% of an aromatic hydrocarbon mixture having a distillation range of 183° to 285°C, 4.0% to 8.0% of an anionic surfactant, 4.0% to 8.0% of an ethoxylated castor oil having 10-60 units of ethylene oxide per molecule and 0 to 2.0% of an antifoam agent.

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